COMMENT

Comment on "On the importance of the free energy for elasticity under pressure"

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Abstract. Marcus et al. (Marcus P, Ma H and Qiu S L 2002 J. Phys.: Condens. Matter 14 L525) claim that thermodynamic properties of materials under pressure must be computed using the Gibbs free energy G, rather than the internal energy E. Marcus et al. state that "The minima of G, but not of E, give the equilibrium structure; the second derivatives of G, but not of E, with respect to strains at the equilibrium structure give the equilibrium elastic constants." Both statements are incorrect.

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Marcus et al. [1] presented an analysis of structural and elastic properties of solids subject to compression under athermal ($T = 0$) conditions. They claim that the Gibbs free energy G must be used at finite pressure P to find the equilibrium structure rather than the internal energy E. In particular, they consider the epitaxial Bain path (EBP) that relates body-centered cubic (bcc), body-centered tetragonal (bct), and face-centered cubic (fcc) structures for Fe at 100 GPa (see also ref. [2]). They show that while $G(c/a; p)$ along the EBP (with a and c the two independent lattice parameters) yields a minimum at $c/a = 1$ (the bcc structure), the minimum of $E(c/a; p)$ along the EBP is displaced, at $c/a = 0.95$. This is a result of misusing elementary thermodynamics [3]. There is a minimum principle for the internal energy E at constant entropy S and volume V, for the enthalpy $H = E + PV$ at constant S and P, for the Helmholtz free energy $A = E - TS$ at constant temperature T and V, and for the Gibbs free energy $G = E - TS + PV$ at constant P and T. There is no minimum principle for E (or H, which are equivalent at $T = 0$, considered by Marcus et al.) at constant P. The correct analysis is shown in Fig. 3 of Stixrude et al. [4], where E versus c/a is shown at constant V for the EBP for Fe, and the extrema are at the bcc structure, as expected. There is nothing wrong with minimizing G at constant P and T, but the exact same results will be obtained for minimizing E at constant V and S. The resulting pressure P can always be obtained from E, since $P = -\frac{\partial E}{\partial V}\big|_S$. At $T = 0$ the constraint $dS = 0$ is trivial, since $S = 0$ at $T = 0$.

Marcus et al. further assert that proper elastic constants must be calculated from second Eulerian strain (ε) derivatives of G (defined as c_{ij} in [1]) rather than the internal energy E ($\bar{c}_{ij}$). Calculating the shear elastic constants $c' = (c_{11} - c_{12})/2$ and c_{44} for bcc-iron using both G and E ($\bar{c}'$ and $\bar{c}_{44}$) they find a shear instability at 150 GPa using G (c') but not for E ($\bar{c}'$), implying that previous computational estimates of elastic constants at pressure are incorrect, and that pressure corrections need to be applied. To the contrary, computation of elastic constants as prescribed by Marcus et al. gives incorrect results. Marcus et al. ignored the fact that the pressure and shear stresses vary as a function of strain. They did not obtain any thermodynamically valid second derivatives by their finite difference procedure, in which they computed $\frac{1}{V_0}\left(E_1(\varepsilon_{ij}) + P_0 V_1(\varepsilon_{ij}) - E_0 - P_0 V_0\right)$; they did not even obtain the derivatives $\frac{1}{V}\frac{\partial^2 G(P)}{\partial \epsilon_i \epsilon_j}\big|_{\epsilon_{k..l}}$, which are not in any case elastic constants, since the pressure and shear stresses vary with their deformation ε_{ij}. This problem remains even if the second order coefficients of a fit for a polynomial expansion in $\frac{1}{V_0}\left(E + P_0 V\right)$ is obtained. The high pressure elastic constants computed using their procedures [2, 5, 6, 7, 8] are incorrect, although the resulting errors may be small in some cases.

It is important to use the appropriate thermodynamic function for the appropriate conditions, and as any student of elementary thermodynamics knows, it is also important to keep track of what is being held constant for a given partial derivative. Elastic constants can be defined by various ways: (1) from the equations of motion (i.e. sound velocities), (2) as derivatives of stress with respect to strain, or (3) as second derivatives of the internal (giving the adiabatic elastic constants) or Helmholtz free

energy (giving the isothermal elastic constants) with respect to strain, holding the other strains constant [9]. Different constants can also be derived depending on the use of finite or infinitesimal strain parameters. All of these definitions are equivalent at zero pressure, but differ under applied stress. The different definitions of elastic constants under applied stress remain sources of confusion [10]. Under no conditions, however, is an elastic constant tensor properly defined as derivatives of H or G with respect to strains, holding the other strains constant.

Kamb [11] even comes to the conclusion that *it is not possible usefully to associate a Gibbs free energy with a non-hydrostatically stressed solid*; this is similarly stated by Wallace [12]. The definition of elasticity on the basis of G is not well-founded. A problem arises, for example, when considering phase equilibria of a fluid in contact with a crystal surface; the chemical potential of components in the fluid in equilibrium with the solid vary according to the crystal face for a stressed solid, indicating there is no unique definition of the Gibbs free energy for a stresses solid [11].

Marcus et al. state that the elastic constants in Refs. [13, 14, 15] are incorrect and require pressure corrections. The elastic constants presented in Refs. [13, 15, 16, 17] are the elastic constants for wave propagation, and these are most easily measured, and are important in seismology and other applications.

For isotropic initial stress the elastic constants for acoustic wave propagation and stress-strain coefficients are equivalent (see section 5 in [9]). We will now illustrate that the expression of strain-energy density can give the same elastic constants as the stress-strain relations for volume conserving strains for a reference state with isotropic applied stress. We use the fourth rank tensor notation from [9] for the elastic constants c_{ijkl} (the stress-strain coefficients). Consider the expression for strain-energy density from Barron and Klein [9]

$$\frac{\Delta E}{V} = -p\varepsilon_{ii} + \frac{1}{2}\left(c_{ijkl} - \frac{1}{2}p\left(2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{jl}\delta_{ik}\right)\right)\varepsilon_{ij}\varepsilon_{kl}, \tag{1}$$

where δ_{ik} is the Kronecker delta. Evaluating this expression, for example, for c_{1313} (corresponding to $\bar{c}_{55} = \bar{c}_{44}$ in Voigt notation, as used in ref. [1]), with the strain

$$\varepsilon(d) = \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix}, \tag{2}$$

with d the strain amplitude, one does indeed obtain a pressure correction term

$$\frac{\Delta E}{V} 2\left(c_{1313} + \frac{1}{2}p\right)d^2. \tag{3}$$

This is the strain used in ref [14], and their elastic constants should consequently be corrected for pressure to obtain wave propagation velocity.

However, by choosing specific volume conserving strains, such as those given in [15, 17], corrections can be avoided. For the c_{1313} example we apply the monoclinic

strain

$$\varepsilon(d) = \begin{pmatrix} 0 & 0 & d \\ 0 & d^2/\left(1-d^2\right) & 0 \\ d & 0 & 0 \end{pmatrix}, \tag{4}$$

eq. 1 becomes

$$\frac{\Delta E}{V} = -\frac{d^2 p}{1-d^2} + 2\left(c_{1313} + \frac{1}{2}p\right)d^2 + \frac{1}{2}c_{2222}\frac{d^4}{(1-d^2)^2} + 2c_{1322}\frac{d^3}{1-d^2}. \tag{5}$$

For hexagonal and tetragonal systems $c_{1322} = 0$ and the final term in the sum on the right hand side is zero. Expanding this into a series of d yields

$$\frac{\Delta E}{V} = \delta^2\left(2c_{1313}\right) + O[\delta^4], \tag{6}$$

without any pressure correction term. This is also true for the other strains given in [15, 17].

Single crystal elasticity is difficult to measure in high pressure experiments, especially for opaque materials such as metals which are discussed in [1]. However, advances in optical spectroscopy have made it possible to measure the Raman active phonon mode in hcp metals. This optical mode and the shear elastic constant c_{1313} can be viewed as properties of the same, nearly continuous phonon branch in an extended Brillouin zone scheme, and can be related by a simple force constant model of phonon dispersion [18]. Results obtained for Fe and Re [15] compare very favorably with experimental estimates [19, 20] over a wide pressure range, corroborating that no pressure correction need be applied. Computed finite temperature elastic constants for Ta [21] also agree well with sound velocities obtained under shock conditions along the Hugoniot.

To conclude, the internal energy E in conjunction with its volume V and strain derivatives defines the thermodynamics and elasticity of a material completely, even under applied stress. Strain derivatives of the Gibbs free energy G, on the other hand, do not yield properly defined elastic constants.

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